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Domain of $CuPt_B$-type and CuAu–I-type ordered structures in highly strained $Cd_xZn_{1-x}Te$/ZnTe heterostructures

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The ordered behaviors in highly strained $Cd_xZn_{1-x}Te$/ZnTe epitaxial layers grown on (001) GaAs substrates were investigated by using selected area electron diffraction pattern (SADP) and cross-sectional high-resolution transmission electron microscopy (HRTEM) measurements. The results of the SADP and the HRTEM measurements showed that CuPt– and CuAu–I-type ordered structures were formed in the $Cd_xZn_{1-x}Te$ epitaxial layers. TEM images showed that the sizes of the ordered domains with elliptical shapes ranged between approximately 10 and 80 nm. An epitaxial relationship between the CuPt– and CuAu–I-type ordered structures was observed. The coexisting behaviors of the two ordered structures and the epitaxial relationship between the structures are discussed. The present results can help to improve the understanding of the formation mechanism and the coexisting behaviors of the two ordered structures in $Cd_xZn_{1-x}Te$ epilayers. [DOI: 10.1063/1.1599966]

Potential applications of II–VI semiconductor thin films in optoelectronic devices operating in the blue-green region of the spectrum have driven an extensive and successful effort to grow $Cd_xZn_{1-x}Te$ layers on various substrates. In particular, $Cd_xZn_{1-x}Te$ epilayers have attracted much attention because of their potential applications for solar cells, light-emitting diodes, and lasers.[1] Some studies concerning several kinds of ordering structures, such as CuAu,[2,3] chalcopyrite,[4,5] and CuPt,[6–8] have been reported in various ternary compound semiconductor epilayers. However, very few works have been done on the formation mechanism for ordered structures in $Cd_xZn_{1-x}Te$ ternary epilayers. The CuPt-type ordered structure in II–VI semiconductor alloys of the composition $A^{II}B^{II}C_2^{VI}$ is described as a short period (AC)/(BC) superlattice with a $\langle 111 \rangle$ orientation.[9] The CuAu–I type ordered structure in II–VI semiconductor alloys of the composition $A^{II}B^{II}C_2^{VI}$ is described as a short period (AC)/(BC) superlattice with a $\langle 001 \rangle$ orientation.[3] Even though many speculative models have been use to describe the formation mechanism for CuPt ordering,[10,11] the origin of the ordering is still unclear. In addition to the role of surface reconstruction, steps at the surface have been reported experimentally to have an influence on the ordering mechanism.[12] Furthermore, studies concerning the domains and the coexistence of CuPt-type and CuAu–I-type ordered structures have not been performed in detail.

This letter reports the domain structure and the coexistent behavior of $CuPt_B$– and CuAu–I-type ordered structures in highly strained $Cd_xZn_{1-x}Te$/ZnTe epilayers grown on ZnTe/GaAs substrates by using molecular beam epitaxy (MBE). The ordering phenomena of the $Cd_xZn_{1-x}Te$ epitaxial layers were characterized by using selected area electron diffraction pattern (SADP) and high-resolution transmission electron microscopy (HRTEM) measurements. The coexisting behavior of the two ordered structures and the epitaxial relationship between the structures are presented on the basis of the results of the SADP and the HRTEM measurements.

Elemental Cd, Zn, and Te with purities of 99.9999% were used as the source materials and were precleaned by repeated sublimation. Cr-doped and semi-insulating (100) GaAs substrates were degreased in warm trichloroethylene (TCE), rinsed in de-ionized water thoroughly, etched in a HF solution, and rinsed in TCE again. As soon as the chemical cleaning process was finished, the GaAs substrates were mounted onto a molybdenum susceptor. Prior to $Cd_xZn_{1-x}Te$/ZnTe epilayer growth, the GaAs substrates were thermally cleaned at 600 °C for 5 min *in situ* in the growth chamber at a pressure of 10^{-8} Torr. The depositions of the $Cd_xZn_{1-x}Te$/ZnTe epilayers were done on GaAs substrates by using the MBE technique at a substrate temperature of 320 °C and at a system pressure of 10^{-6} Torr. The source temperatures of the Cd, Zn, and Te sources were 160, 250, and 320 °C, respectively, and the typical growth rates for the $Cd_xZn_{1-x}Te$ and ZnTe were 0.2 and 0.5 μm/h, respectively. After the $Cd_xZn_{1-x}Te$ thin films had been grown, the samples were annealed at the growth temperature for 5 min to stabilize the thin layer. The typical thickness of the $Cd_xZn_{1-x}Te$ film was approximately 800 nm.

Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM 3010 transmission

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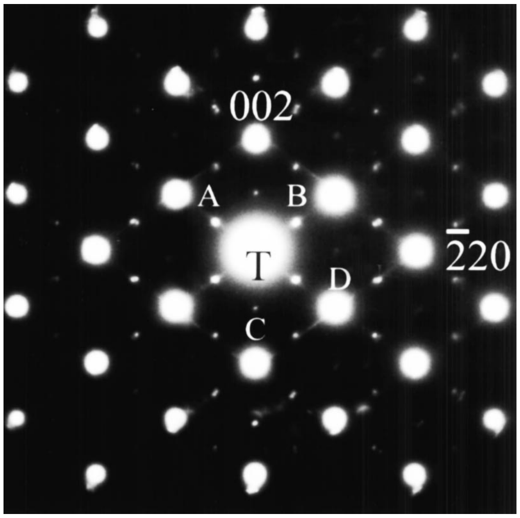

FIG. 1. Selected area electron diffraction pattern of the $Cd_{0.76}Zn_{0.24}Te$ epilayer showing two symmetric sets of {1/2 1/2 1/2}, {001} and {110} extra spots along the [110] zone axis. The {1/2 1/2 1/2} extra spots, marked by A and B, are attributed to $CuPt_B$-type ordering. The superstructure reflections located in the {001} and the {110} planes, marked by C and D, are typically related to CuAu–I-type ordered structures.

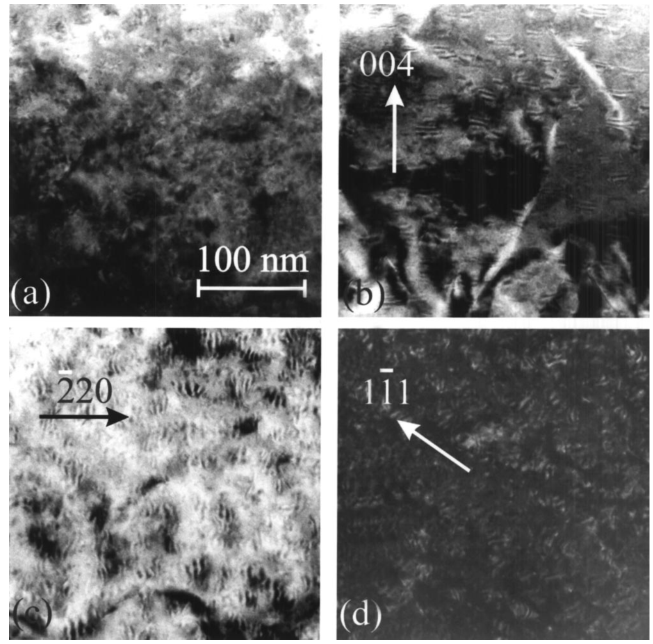

FIG. 2. Transmission electron microscopy micrographs showing the ordered domain structures in $Cd_{0.76}Zn_{0.24}Te$ epitaxial layers grown on ZnTe buffer layers: (a) zone axis, (b) [004], (c) $[\bar{2}20]$, and (d) [111].

electron microscope operated at 300 kV. The samples for the TEM measurements were prepared by cutting and polishing with a diamond paper to a thickness of approximately 30 μm and then by argon-ion milling at liquid-nitrogen temperature to electron transparency.

Figure 1 shows a SADP obtained from a $Cd_{0.76}Zn_{0.24}Te$ epitaxial layer grown on a ZnTe buffer layer. While the fundamental zinc-blende spots were seen along the [110] zone axis, $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$, {001}, and {110} superstructure reflections, together with fundamental zinc-blende spots, were observed along the [110] zone axis, as shown in Fig. 1. The $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ extra spots are attributed to the $CuPt_B$ type ordering typically observed in III–V compound semiconductors.[5] An unequivalent crystallographic atomic arrangement of four {111} planes distinguishes the $CuPt_A$ and the $CuPt_B$ ordered structures from each other. The $CuPt_A$ ordered structure is related to the (111) and the (111) planes and generates $(h\pm\frac{1}{2},k\pm\frac{1}{2},l\pm\frac{1}{2})$ and $(h\mu\pm\frac{1}{2},k\mu\frac{1}{2},l\pm\frac{1}{2})$ extra spots in the SADP. The $CuPt_B$ ordered structure, which produces $(h\pm\frac{1}{2},k\mu\pm\frac{1}{2},l\pm\frac{1}{2})$ and $(h\mu\pm\frac{1}{2},k\pm\frac{1}{2},l\pm\frac{1}{2})$ superstructure reflections, is thought to exist in the (111) and the (111) planes. The $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$ extra spots denoted by A and B in Fig. 1 have almost the same intensity, and their shapes are not sharp, but slightly diffusive. This result indicates that the formation of perfect ordering is not possible in $Cd_xZn_{1-x}Te$ epilayers. The superstructure reflections located in the {001} and the {110} planes, marked by "C" and "D," are typically related to CuAu–I-type ordered structures. The (hkl) spots, which satisfy the conditions $h+k=$even and $k+l=$odd, are only observed in the CuAu–I-type ordered structure along the [110] zone axis.[2] Even though the {001} and the {110} superstructure reflections might generally originate from double diffraction of the $CuPt_B$ ordered structures, this description cannot explain the earlier behavior. Since CuAu–I-type ordered structures are observed in the HRTEM images, they produce a doublet periodicity along the [001] and the [110] directions. The intensity of the superstructure reflection C for the CuAu–I-type ordered structure is stronger than that for the superstructure reflection D. This behavior implies that the existence probability of the {001} double periodicity is larger than that of the {110} double periodicity. The intensities of the superstructure reflections for the CuAu–I-type ordered structure are weaker than those for the $CuPt_B$-type ordered structure. This behavior implies that the existence probability of the $CuPt_B$-type ordering is larger than that of the CuAu–I-type ordering.

Figure 2 shows cross-sectional TEM images obtained from a $Cd_{0.76}Zn_{0.24}Te$ epitaxial layer grown on a ZnTe buffer layer. The bright-field image in the Fig. 2(a) was taken from the zone axis, and the bright-field images in Figs. 2(b) and 2(c) were taken under the two-beam condition. The dark-field image in Fig. 2(d) was under from the [111] two-beam condition. Partially ordered domain structures were clearly observed for the $Cd_xZn_{1-x}Te$ epilayers, as shown in Fig. 2. The partially ordered domains were uniformly distributed in the $Cd_xZn_{1-x}Te$ epilayer. The sizes of the partially ordered domains ranged approximately from 10 to 80 nm. Therefore, these partially ordered domains might lead to the formation of quantum dots as Kops *et al.* suggested for GaInP alloys.[13]

Figure 3 shows a HRTEM image along the [110] zone axis, and the image has a doublet periodicity in the contrast of the {111} lattice planes of the $Cd_{0.76}Zn_{0.24}Te$ epitaxial layer grown on a ZnTe buffer layer. The doublet periodicities seen in Fig. 3, which exist in the (111) and the (111) planes, are similar to the superstructure reflections in the SADP shown in Fig. 1. The doublet periodicity in the contrast of the (111) lattice plane is related to the $CuPt_B$ ordering, and that of the (111) lattice planes is attributed to $CuPt_A$ ordering. The ordered domains marked by A, B, E, F, and G in Fig. 3 consist of two overlapping $CuPt_B$-type ordered structure with a 180° rotation. In Fig. 3, antiphase boundaries for the $CuPt_B$-type ordering, which are marked by "APB," exist be-

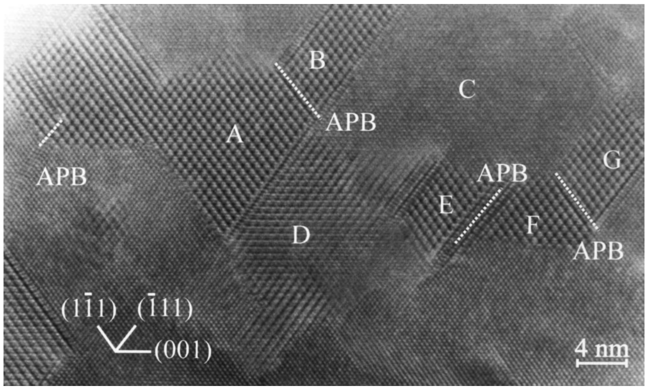

FIG. 3. Cross-sectional high-resolution transmission electron microscope image of the $Cd_{0.76}Zn_{0.24}Te$ epilayer showing an ordered structure having a doublet periodicity on the {111} and the {001} lattice planes. Two different variants can be seen along the ⟨111⟩ direction. The doublet periodicity in the [001] direction is seen in the C region. Antiphase boundaries existing between $CuPt_B$-type ordered domains are indicated by APB.

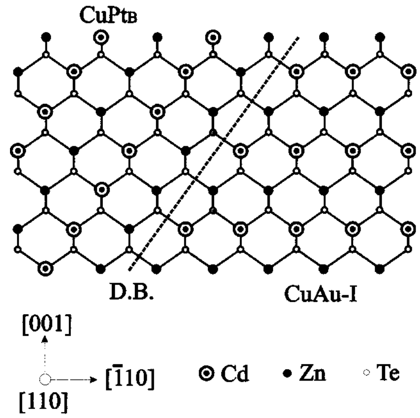

FIG. 4. Schematic diagram of the epitaxial relationship between the $CuPt_B$-type and the CuAu–I-type ordered structure in $Cd_xZn_{1-x}Te$ epilayers along the [110] projection. A domain boundary is indicated by D.B.

tween $CuPt_B$-type ordered domains in Fig. 3. The antiphase boundaries are located along the ⟨111⟩ directions and cause streak lines along the ⟨111⟩ direction in the SADP. However, antiphase boundaries in III–V ordered structures cause the streak lines to become wavy and diffusive.[14] The well-defined $CuPt_B$-type ordered domains consist of the domain boundaries between the {111} and the {001} planes. The sizes of the $CuPt_B$-type ordered domains are approximately between 10 and 80 nm. The doublet periodicity in the contrast of the {001} lattice planes, which is typically considered to be due to a CuAu–I-type ordering, is related to the diffraction spots marked by C in Fig. 1. The doublet periodicities corresponding to the $CuPt_B$ ordering, which are formed at the $(1\bar{1}1)$ and the $(\bar{1}11)$ planes, are more dominant than those of the (001) plane related to the CuAu–I-type ordering, and they are extensively distributed. The CuAu–I-type ordered domains marked by C in Fig. 3 neighbor the $CuPt_B$-type ordered domains marked by ‘‘B.’’ Half of the CuAu–I-type ordered domain is surrounded by $CuPt_B$-type ordered domains. The thickness of the domain boundaries is very thin. The ordered domain marked by D consists of overlapping or mixed CuPt-type and CuAu–I-type ordered structure.

Since the regions B and C of Fig. 3 show an epitaxial relationship between the CuAu–I-type ordered structure and the $CuPt_B$-type ordered structure, a possible schematic diagram can be proposed for the epitaxial relation between the CuAu–I-type ordered structure and the $CuPt_B$-type ordered structure, as shown in Fig. 4. An epitaxial relation between the CuAu–I-type and the $CuPt_B$-type ordered structures can be determined because the calculated lattice constants for the CuAu–I-type ordered structure and the $CuPt_B$-type ordered structure are the same.[15] The domain boundary between the CuAu–I-type ordered structure and the $CuPt_B$-type ordered structure is marked by ‘‘D.B.’’ in Fig. 4. This behavior is in reasonable agreement with the epitaxial relationship shown in Fig. 3.

In summary, the results of the SADP and the HRTEM measurements on $Cd_xZn_{1-x}Te$ epitaxial layers grown on (001) ZnTe buffer layers showed the coexistence of CuPt- and CuAu–I-type ordered structures. The SADP showed two sets of $\{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$, {001}, and {110} superstructure reflections with almost symmetric intensities along the [110] zone axis; no superstructure reflections were seen along the $[1\bar{1}0]$ zone axis. The observed ordered structure had the typical features of two variations of $CuPt_B$-type ordering superposed on two variations of CuAu–I-type ordering along the [110] zone axis. An antiphase boundary was observed in the CuPt-type ordered structure of the $Cd_xZn_{1-x}Te$ epitaxial layer. A possible atomic arrangement for the ordered structure was described on the basis of the experimental results. These present observations can help improve understanding of the microstructural properties in $Cd_xZn_{1-x}Te/ZnTe$ epilayers grown on GaAs substrates.

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[1] A. Cavallini, B. Fraboni, W. Dusi, M. Znarini, and P. Siffert, Appl. Phys. Lett. **77**, 3212 (2000).
[2] T. W. Kim, D. U. Lee, H. S. Lee, J. Y. Lee, and M. D. Kim, J. Appl. Phys. **89**, 2503 (2001).
[3] T. S. Kuan, W. I. Wang, and E. L. Wilkie, Appl. Phys. Lett. **51**, 51 (1987).
[4] O. Ueda, T. Fujii, Y. Nakada, H. Yamada, and I. Umebu, J. Cryst. Growth **95**, 38 (1989).
[5] A. Zunger and S. Mahajan, *Handbook on Semiconductors*, edited by S. Mahajan (North-Holland, Amsterdam, 1994), Vol. 3, p. 1399.
[6] T. W. Kim, D. U. Lee, D. C. Choo, H. S. Lee, J. Y. Lee, and H. L. Park, Appl. Phys. Lett. **78**, 922 (2001).
[7] H. S. Lee, J. Y. Lee, T. W. Kim, and H. L. Park, J. Cryst. Growth **233**, 749 (2001).
[8] H. S. Lee, J. Y. Lee, T. W. Kim, D. U. Lee, D. C. Choo, and H. L. Park, J. Appl. Phys. **90**, 4027 (2001).
[9] M. S. Kwon and J. Y. Lee, J. Cryst. Growth **191**, 51 (1998).
[10] J. E. Bernard, S. Froyen, and A. Zunger, Phys. Rev. B **44**, 11178 (1991).
[11] S. B. Zhang, S. Froyen, and A. Zunger, Appl. Phys. Lett. **67**, 3141 (1995).
[12] H. Murata, I. H. Ho, Y. Hosokawa, and G. B. Stringfellow, Appl. Phys. Lett. **68**, 2237 (1996).
[13] U. Kops, R. G. Ulbrich, M. Burkard, C. Geng, F. Scholz, and M. Schweizer, Phys. Status Solidi A **164**, 459 (1997).
[14] A. Gomyo, T. Suzuki, and S. Iijima, Phys. Rev. Lett. **60**, 2645 (1988).
[15] S.-H. Wei, L. G. Ferreira, and A. Zunger, Phys. Rev. B **41**, 8240 (1990).